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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C01B 17/00, B01J 23/32, D21C 11/00, 3/16, 3/00	A1	(11) International Publication Number: WO 97/19891 (43) International Publication Date: 5 June 1997 (05.06.97)
(21) International Application Number: PCT/US96/14402 (22) International Filing Date: 6 September 1996 (06.09.96) (30) Priority Data: 08/565,087 30 November 1995 (30.11.95) US (71) Applicant: QUANTUM TECHNOLOGIES, INC. [US/US]; 1632 Enterprise Parkway, Twinsburg, OH 44087 (US). (72) Inventors: HURST, Marilyn, M.; 1890 Stoney Hill Drive, Hudson, OH 44236 (US). BUTLER, Kevin, P.; 1753 Nova Lane, Youngstown, OH 44514 (US). YANT, Robert, E.; 6849 River styx Road, Medina, OH 44256 (US). GALLUCH, Richard, J.; 7211 Huntington Road, Hudson, OH 44236 (US). (74) Agent: CENTANNI, Michael, A.; 7335 Beresford Avenue, Parma, OH 44130 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: NOVEL CATALYST FOR THE OXIDATION OF SULFIDES (57) Abstract A novel catalyst has been developed for increasing the rate of oxidizing sulfides, particularly sulfides present in pulping liquor and, in turn, improving the efficiency in paper pulping processes. According to the invention, a sulfide containing pulping liquor is contacted with a catalyst system comprising oxides of manganese wherein the majority of the particles of the catalyst has a size of 45 microns or smaller. The oxides of manganese may optionally be used in combination with compounds of scandium, yttrium, rare earth metals, Al, Fe, Ni, Cr, and Co.		

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Title: NOVEL CATALYST FOR THE OXIDATION OF SULFIDES

Field of the Invention

This invention relates to a catalyst for the oxidation of sulfides and particularly for the sulfide oxidation process of pulping liquor. More specifically, a catalyst for oxidizing sulfides at a substantially increased rate of conversion has been developed wherein the catalyst comprises oxides of manganese in a relatively fine particulate solid.

Background of the Invention

Sulfides are present and utilized for a variety of reasons in the fluid streams of industrial processes. It is often necessary to oxidize the sulfides present in such fluid streams to, for example, polysulfides for their ultimate effective end use and/or removal.

The use of polysulfide, for example, in the pulping of wood to produce paper is known. For example, U.S. Patents 3,470,061; 3,653,824; and 3,860,479 disclose various processes and catalysts for the formation of polysulfide by treating a sulfide containing pulping liquor with an oxidizing catalyst. These patents describe the use of oxides of manganese as the oxidizing catalyst to form polysulfides and process techniques for the regeneration of the catalyst. The processes disclosed in these patents require from at least one half hour up to several hours to achieve substantial conversion of the sulfide to polysulfide.

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Manganese oxide and permanganate catalysts for applications in gaseous streams, such as oxidation and deodorization of exhaust gases from paint drying ovens, are described in U.S. Patents 4,290,923; 4,299,735; 4,321,240; and 5,260,248. None of these disclosures describe the use of such catalysts for the oxidation of sulfides and particularly in the sulfide oxidation process for pulping liquor.

While various catalyst systems and processes have been developed for oxidizing sulfides and particularly sulfides to polysulfide, there is need for a catalyst system that will significantly increase the rate of the oxidation of a sulfide to polysulfide.

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Summary of the Invention

According to the present invention, a catalyst for the oxidation of sulfides is provided for substantially increasing the rate of conversion of the sulfides, e.g., to polysulfide, wherein the catalyst comprises oxides of manganese and wherein about 68% of the total weight of the catalyst have a particle size of about 45 microns or smaller.

Further in accordance with the present invention, a catalyst for substantially increasing the rate of oxidizing sulfides present in a pulping liquor sulfide oxidation process is provided.

Still further in accordance with the present invention, a process is provided for oxidizing sulfides present in a pulping liquor sulfide oxidation process at a substantially increased rate by contacting a pulping liquor comprising sulfides with a catalyst system comprising oxides of manganese in a catalytic effective amount wherein about 68% of the total weight of the catalyst system has a particle size of about 45 microns or smaller.

Still further in accordance with the present invention, a catalyst for the oxidation of sulfides present in a system is provided wherein the catalyst system comprises the oxides of manganese in combination with compounds of cerium, lanthanum, scandium, yttrium, aluminum, iron, nickel, chromium, zinc, or cobalt.

Still further in accordance with the present invention, a catalyst system for the oxidation of sulfides is provided wherein the catalyst will

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convert up to about 95% of the sulfides present in a system within about 15 minutes.

These and other aspects of the present invention will be appreciated upon the reading and understanding of the specification.

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DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

A catalyst composition providing an unexpected increase in the rate of oxidation of sulfides has been developed. The use of polysulfides for pulping of wood to be formed into paper products is known as well as the in situ formation of polysulfides from monosulfides as described in the Barker patents discussed above. The processes described in the Barker patents, however, require generally one and one half to four hours to achieve up to 80% conversion of monosulfide to polysulfide. The catalyst and method of the present invention achieves up to 95% by weight conversion of monosulfide to polysulfide within 10 to 15 minutes and usually within 2 to 3 minutes.

It has been found that the catalyst composition according to the present invention preferably include oxides of manganese either employed alone or in combination with other metal compounds. For the purposes of the present invention, preferred oxides of manganese include those oxides which are generally capable of reduction. By way of example, such oxides of manganese may include, MnO_2 , MnOOH , Mn_3O_4 , Mn_2O_3 , and the like as well as the mixtures of these different oxides of manganese. For the purposes of the present invention, MnO_2 is most preferred and may be admixed with minor amounts of other oxides of manganese.

It is further preferred in accordance with the present invention, that the oxides of manganese are activated, e.g., the ore or separated oxides are acid treated or treated with caustic followed by washing and/or bleaching of the treated material. Activated oxides of manganese are

commercially available and described in the patent literature. For example, activated oxides of manganese having the desired particle size range within the scope of the invention are commercially available through such sources as Carus Corporation, Eagle-Pitcher, Aldrich and the like. Exemplary activated oxides of manganese useful within the scope of the present invention are described in U.S. Patent No. 4,290,923; 4,299,735; 4,321,240; and 5,260,248 which disclosures are herein incorporated by reference for their teachings directed to activated oxides of manganese. It is pointed out, however, that good conversion rates have been obtained with non-activated oxides of manganese.

In another embodiment of the present invention, the oxides of manganese may be used in combination with one or more metal compounds. For example, the oxides of manganese may be used in combination with the compounds of such metals as cerium, lanthanum, scandium, yttrium, nickel, aluminum, iron, chromium, zinc and cobalt. The oxides or sulfides of these metals are preferably employed in combination with the oxides of manganese. It has been found that combinations of the oxides of manganese in combination with cerium compounds and optionally aluminum compounds are particularly useful in the present invention. In one embodiment the catalyst of the present invention may comprise one of the following components or combinations. MnO_2 ; MnO_2 and Ce_2O_3 ; and MnO_2 , Ce_2O_3 and Al_2O_3 . While the relative amounts of the different metal compounds making up the catalyst of the present invention is not particularly critical and, as previously mentioned, the oxides of manganese may comprise up to 100% by weight of the catalyst, it has been found that the manganese oxides may comprise from about 37% by weight up to 100% by weight of the total catalyst composition where the balance is made up by other metal compounds. When a third

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metal compound is employed in the catalyst composition, e.g., Al_2O_3 , it is found that this third metal compound may be present preferably in the range of about 12% by weight to about 18% by weight of the total weight of the catalyst composition.

According to the present invention, a significant improvement in the rate of oxidation of sulfides present in a system has been produced. It has been found that up to about 95% by weight of the monosulfide present in a system may be oxidized within about 10 to about 15 minutes and more typically within about 2 to 3 minutes. This improvement in rate of oxidation has been achieved by employing the catalyst described above wherein about 68% by weight of the catalyst has a particle size of 45 microns or smaller and preferably an oxide of manganese having a particle size of 20 microns or smaller. It previously has been disclosed and taught that only catalysts having much larger particle sizes are useful for such reaction systems. Any known techniques in the industry may be employed to classify the catalyst particles to obtain the desired particle size range.

Typically the polysulfides used in, e.g., the pulping of paper, are sodium sulfides such as Na_2S_2 and may be formed in situ from Na_2S . However, the monosulfide may be present in other forms including inorganic or organic monosulfides capable of oxidation to a polysulfide.

The catalyst in accordance with the present invention is generally useful for a temperature range of a monosulfide containing solution of about 50°C to about 90°C which is typically the temperature range of the white liquor from the pulping of wood. However, the oxidation reaction

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may be carried out at a range of temperatures, for example, at room temperature to over 100°C.

The oxidation of the monosulfide may, in general, be carried out by contacting the monosulfide containing solution with the catalyst of the present invention, agitating the monosulfide solution containing catalyst and recovering the resultant oxidation product. The oxidation may further be conducted in the presence of air, pure oxygen, or an increased oxygen mixture in air.

Thus, the process according to the present invention not only provides the advantages of previously developed in situ processes by avoiding a separate addition of sulfur and polysulfides to pulping liquor, the present invention provides for a process that may be conducted and concluded within a few minutes as opposed to about an hour or more and, in turn, improving upon the economics of such industrial processes as the pulping of paper. For the purposes of the present invention, it has been found that the amount of catalyst that may be used to oxidize a monosulfide to polysulfide may range from about 1% by weight to about 20% by weight of the reactive composition.

The following examples are presented to illustrate the present invention and are not to be considered to limit the scope of the present invention where such scope is set out in the claims.

EXAMPLE I

For this example, 300 g of hot (70°C) white liquor is poured over a catalyst of MnO_2 , Ce_2O_3 and Al_2O_3 wherein at least about 68% by weight

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of the catalyst has a particle size of about 20 microns or smaller and stirred for two (2) minutes. A second solution of 100 g of hot (70°C) white liquor is poured over a MnO_2 bed wherein at least about 68% by weight of the catalyst has a particle size of 74 microns or larger and stirred for two (2) minutes.

The following Table I sets out the results from these two runs.

TABLE I

<u>CATALYST</u>	<u>Na_2S</u>	<u>Polysulfide sulfur g/L</u>
Carulite 100®	13.95g/L	4.8g/L
MnO_2 (large particle size)	26.4g/L	0.96g/L

EXAMPLE II

In this example, several runs were conducted with an MnO_2 catalyst where at least about 70% by weight of the catalyst had a particle size of 44 microns or smaller. The same procedure for this example was followed as in Example I however in each instance 200g of white liquor having a temperature of 80°C was employed and stirred for two (2) minutes. The results for these runs are set out in Table II.

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TABLE II

<u>g of MnO₂ used</u>	<u>Na₂S g/L</u>	<u>Polysulfide g/L</u>
4g	13.02	4.08
8g	4.8	6.52
10g	3.56	7.00

EXAMPLE III

For this example, the same procedure described in Example I was followed for this example. In this example 5g of Carulite 100[®] was contacted with 200g of white liquor at room temperature and stirred for 40 seconds. The Na₂S concentration was 7.9 g/L and final polysulfide was determined to be 6.96 g/L.

EXAMPLE IV

As a comparison to Example III, 10g of MnO₂ having a particle size range of 62 microns to 250 microns was contacted with 200g of white liquor at temperatures of 60°C for 40 seconds and the polysulfide content was determined. The results showed that the original Na₂S was 24.2 g/l and final polysulfide was determined to be 0.48 g/L.

EXAMPLE V

In this example an activated MnO₂ catalyst having a particle size of primarily less than 5 microns is used to produce a polysulfide from Na₂S and is compared to an MnO₂ catalyst having particle sizes in the range of 62 microns to 250 microns. In both runs 6.26g of the catalyst is contacted with 200g of white liquor at 80°C and stirred for 2 minutes. The results of this example is set out in Table III below.

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TABLE III

	<u>Na₂S g/L</u>	<u>S g/L</u>
MnO ₂ have particle size in range of 62 microns to about 200 microns	23.0	0.64
Activated MnO ₂ Particles sizes 5 microns or smaller	5.58	8.72

EXAMPLE VI

For this example, the same procedure described in Example I was followed for this example. In this example, 6.0 grams of non-activated MnO₂ wherein at least about 68% by weight of the MnO₂ had a particle size of 5 microns or smaller was contacted with 200g of white liquor having a temperature of 80°C. The white liquor containing the above described MnO₂ was stirred for 2 minutes and the polysulfide content was determined to be 8.16g/L with the final Na₂S concentration determined to be 4.11g/L.

EXAMPLE VII

For this example, essentially the same procedure described in Example I was followed for this example except the polysulfide content was determined at regular timed intervals. the same catalyst as described in Example II was employed where the reaction was carried out in the first instance in the presence of oxygen under pressure and in the second instance in the presence of air under pressure. The trial run in O₂ is set out in Table IV below while the trial run in air is set out in Table V below.

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TABLE IV

<u>Time in seconds</u>	<u>Na₂S g/L</u>	<u>Polysulfide g/L</u>
15	16.43	4.8
30	12.56	6.4
60	6.51	6.96
120	3.88	5.4

For this run 720 g of white liquor at 80°C was contacted with 5% catalyst concentration by weight. The O₂ was maintained at 77 PSIG.

As can be observed from the above results, good results are obtained even after only 30 seconds.

TABLE V

<u>Time in seconds</u>	<u>Na₂S g/L</u>	<u>Polysulfide g/L</u>
5	8.37	5.56
10	5.27	7.0
15	4.19	6.48
20	3.79	5.68
30	2.33	4.88
60	3.1	5.6

For this run in air 25.11g/L of Na₂S in white liquor was employed at 80°C with an air pressure of 56 PSIG

Other features and aspects of this invention will be appreciated by those skilled in the art upon reading and comprehending this disclosure. Such features, aspects and expected variations and modifications of the reported results and examples are clearly within the scope of this

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invention where the invention is limited solely by the scope of the following claims.

What is claimed is:

1. A catalyst for the oxidation of sulfides to substantially increase the rate of conversion of sulfides wherein said catalyst comprises oxides of manganese and wherein about 68% of the total weight of said catalyst has a particle size of about 45 microns or smaller.
2. The catalyst according to claim 1 wherein said catalyst system comprises oxides of manganese in combination with compounds of cerium, lanthanum, scandium, yttrium, aluminum, iron, chromium, zinc, cobalt, or nickel.
3. The catalyst according to claim 2 wherein said catalyst comprises MnO_2 , and Ce_2O_3 .
4. The catalyst according to claim 3 wherein said catalyst comprises MnO_2 , Ce_2O_3 , and Al_2O_3 .
5. The catalyst according to claim 1 wherein said catalyst will convert upto at least about 65% of sulfides present in a system within about 10 minutes.
6. The catalyst according to claim 1 wherein said oxides of manganese are activated and present in the catalyst within the range of about 37% to about 99% by weight of the total weight of the composition.
7. The catalyst according to claim 2 wherein said metal compound selected from the metals of aluminum, chromium, nickel, iron and cobalt is

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present in the system within the range of about 12% to about 18% based on the total weight of the catalyst.

8. The catalyst according to claim 1 wherein about 1% to about 20% by weight, of the catalyst system is utilized to oxidize said sulfide compositions.
9. The catalyst according to claim 1 wherein 68% by weight of said catalyst has a particle size of 10 microns or less and will convert up to about 95% of sulfides present in a system within about 3 minutes.
10. A catalyst for substantially increasing the rate of oxidizing sulfides present in pulping liquor sulfide oxidation process comprising oxides of manganese in a catalytic effective amount and wherein about 68% by weight of said oxides of manganese have a particle size of about 45 microns or smaller.
11. The catalyst according to claim 10 wherein said catalyst system comprises oxides of manganese in combination with compounds of cerium, lanthanum, scandium, yttrium, aluminum, iron or nickel.
12. The catalyst according to claim 11 wherein said catalyst comprises MnO_2 , and Ce_2O_3 .
13. The catalyst according to claim 12 wherein said catalyst comprises MnO_2 , Ce_2O_3 and Al_2O_3 .

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14. The catalyst according to claim 10 wherein substantially all the sulfides present in the pulping liquor will be oxidized by said catalyst system within about five minutes.
15. The catalyst according to claim 10 wherein said oxides of manganese are activated and present in the catalyst within the range of about 37% to about 99% by weight of the total weight of the catalyst.
16. The catalyst according to claim 10 wherein said metal compound selected from the metals of aluminum, mercury, nickel, iron and cobalt is present in the catalyst within the range of about 12% to about 18% based on the total weight of the catalyst.
17. The catalyst according to claim 10 wherein about 1% to about 20% by weight, of the catalyst is utilized to oxidize said sulfide compositions.
18. The catalyst according to claim 10 wherein the particle size of 68% by weight of said catalyst is 10 microns or less and will oxidize substantially all of said sulfides in said pulping liquor within about 3 minutes.
19. A process for oxidizing sulfides present in a pulping liquor sulfide oxidation process at a substantially increased rate comprising contacting a pulping liquor comprising sulfides with a catalyst comprising oxides of manganese in a catalytic effective amount wherein about 68% of the total weight of said catalyst has a particle size of 45 microns or smaller.

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20. The process according to claim 19 wherein said catalyst system comprises oxides of manganese in combination with oxides of cerium, lanthanum, scandium, yttrium, aluminum, copper, iron or nickel.
21. The process according to claim 20 wherein said catalyst comprises MnO_2 , and Ce_2O_3 .
22. The process according to claim 21 wherein said catalyst comprises MnO_2 , Ce_2O_3 , and Al_2O_3 .
23. The process according to claim 19 wherein substantially all the sulfides present in the pulping liquor will be oxidized by said catalyst system within about five minutes.
24. The process according to claim 19 wherein said oxides of manganese are present in the catalyst within the range of about 37% to about 99% by weight of the total weight of the catalyst.
25. The process according to claim 19 wherein said metal compound selected from the metals of aluminum, mercury, nickel, iron and cobalt is present in the catalyst within the range of about 12% to about 18% based on the total weight of the catalyst.
26. The process according to claim 19 wherein about 1% to about 20% by weight, of the catalyst is utilized to oxidize said sulfide compositions.
27. The process according to claim 19 wherein said contacting is achieved by mixing said catalyst with a sulfide containing pulping liquor

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at a temperature up to about 100°C for a time of less than about fifteen minutes.

28. The process according to claim 19 wherein the particle size of 68% by weight of said catalyst is 10 microns or less and will oxidize said sulfides in said pulping liquor within about 3 minutes.

INTERNATIONAL SEARCH REPORT

 International application No.
 PCT/US96/14402
A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C01B 17/00; B01J 23/32; D21C 11/00, 3/16, 3/00

US CL : 423/562; 502/324; 162/29, 65, 81, 82

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 423/562; 502/324; 162/29, 65, 81, 82

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 3,860,479 A (BARKER et al) 14 January 1975, abstract.	1-28
Y	US 3,470,061 A (BARKER) 30 September 1969, abstract.	1-28
Y	US 3,653,824 A (BARKER et al) 04 April 1972, cols. 5-6 and col. 7, lines 30-75.	1-28
Y	US 4,290,923 A (MEIN et al) 22 September 1981, abstract.	1-28
Y	US 4,024,229 A (Smith et al) 17 May 1977, col. 9.	1-28

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

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10 NOVEMBER 1996

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